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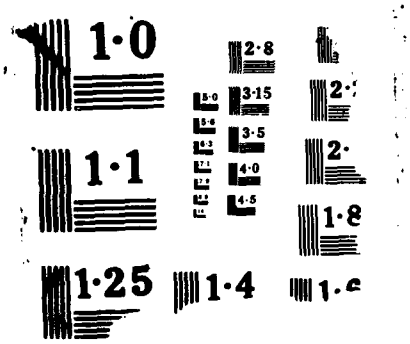
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19 ABSTRACT (Continue on reverse if necessary and identify by block number)

Basal X-ray diffraction patterns of mixed-layered illite/smectite minerals have been calculated using the fundamental particle concept of Nadeau and co-workers. The patterns are more realistic than those computed according to Markovian statistics, which is the standard method at present. These findings at least partly confirm the hypothesis of Nadeau and co-workers, and suggest that they may be correct in interpreting the smectite to illite transformation as one of dissolution and reprecipitation, instead of the conventional one of layer-by-layer transformation.

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THE CRYSTAL STRUCTURE OF ILLITE/SMECTITE

FINAL REPORT

R. C. REYNOLDS JR.

APRIL 1, 1988

U. S. ARMY RESEARCH OFFICE

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THE VIEW, OPINIONS, AND/OR FINDINGS CONTAINED IN THIS REPORT ARE THOSE OF THE AUTHOR AND SHOULD NOT BE CONSTRUED AS AN OFFICIAL DEPARTMENT OF THE ARMY POSITION, POLICY, OR DECISION, UNLESS SO DESIGNATED BY OTHER DOCUMENTATION.

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INTRODUCTION

X-ray diffraction patterns of mixed-layered illite/smectite are interpreted by comparisons with patterns calculated for different structural and chemical parameters. The dominant factors that control the character of the one-dimensional, basal or 00*l* diffraction series, are the proportions of illite and smectite, their layer thicknesses (d(001)), and the patterns or lack thereof in the stacking sequence of these two layer types along the z direction. The layer thicknesses are easily obtained by independent studies, so the proportion and stacking statistics for the layer types are the critical parameters for characterization of a given mixed-layered mineral.

The structures of mixed-layered illite/smectites were first explained by Reynolds and Hower (1970), and the complete algorithm for calculating diffraction patterns was discussed by Reynolds (1980). Over the years, many investigators have had success in correlating diffraction patterns, interpreted by these methods, with geological occurrence and structural data obtained by other experimental means. The first, and most important of these was the work of Perry and Hower (1970). Recently, however, diffraction patterns have been obtained that show subtle but irreconcilable departures from the theory. The difficulties are most noticeable for illite/smectites that are illite-rich and ordered according to long-range patterns.

The published results of Nadeau and co-workers (*e.g.* Nadeau *et al.*, 1984) suggest that illite/smectite consists of fundamental illite packets, 20,30,--*etc*. Å thick that absorb water or ethylene glycol at their interfaces and thus act as ordered stacks of illite separated by smectite-like interlayers. The long-range order, or Reichweite, thus is seen as a consequence of the thicknesses and relative proportions of these illite particles. The stacks of illite particles are aligned sufficiently well to act as coherent scattering domains for X-ray diffraction, as Nadeau *et al.* demonstrated experimentally. Their work is of fundamental importance in explaining the chemical- geologic mechanisms for the transformation of smectite to illite.

In the older model (Reynolds and Hower, 1970), the transformation was seen as a layer-by-layer transformation of smectite to illite. The existence of nearest-neighbor ordering, leading to the unit cell sequence ISISIS--*etc*., was difficult to explain by such a mechanism. More difficult was the explanation of

long- range ordering (Reichweite = 3 or R=3) which leads to the sequence, for example, of IIISIIISIIISIIIS--- *etc*.

In the Nadeau model, the long-range ordering is explained by the presence of fundamental particles that contain three illite unit cells, and that produce a smectite-like interface by the absorption of water or glycol. For this structural model, the Reichweite is seen as simply the thickness of the individual illite fundamental particles. The transformation of smectite to illite consists of the growth of large particles at the expense of smaller ones by a mechanism such as Ostwald crystal ripening. Since the proposal was written to ARO for this research, independent experimental evidence has tended to validate the model of Nadeau and his co-workers. The most significant, in the writer's opinion, of the recent studies are the results of Whitney (1988) who studied the transformation by hydrothermal synthesis in the laboratory and demonstrated, by means of oxygen isotopes, that equilibration with the liquid occurred at the point of ordering, that is, when the Nadeau-type fundamental particles began to grow. Inoue *et al*. (1987), studied the textural changes, by means of electron microscopy, and diffraction characteristics of illite/smectite, over a range of compositions for natural hydrothermal occurrences. They observed the morphologically distinct fundamental particles suggested by Nadeau and his co-workers, and documented the growth of these over the course of the reaction.

THE PROBLEM STUDIED

The research reported upon here was centered on the calculation of X-ray diffraction patterns for illite/smectite structures that are based on the fundamental particle concept of Nadeau and his co-workers. If such patterns are more realistic then those based on the older or Markovian statistics used by Reynolds (1980), that result constitutes good circumstantial evidence for the validity of the fundamental particle concept. In addition, a modified and improved computer algorithm will enhance the abilities of others in the field to characterize mixed-layered illite/smectite.

The basic mathematical approach is identical for the two models (Markovian and fundamental particle), but the frequency of occurrence of scattering vectors differs between the two. The basic diffraction equation is an inverse Patterson function, often called the lattice-sum technique (Ergun, 1970).

$$I = N(P_I|G_I|^2 + P_S|G_S|^2) + 2\sum_S G_h G_k \sigma_S \exp(-R_S/\delta)\cos(\phi R_S) \qquad (1)$$

where $\phi = 4\pi\sin\theta/\lambda$

The summation is taken over all spacings, S, that are made up of some combination or permutation of the two layer types taken two at a time, three at a time ----N at a time. N is the number of unit cells in a crystallite, P_I and P_S refer to the decimal proportions of illite and smectite, G_I and G_S are the amplitudes of scattering of the two types of unit cells in the direction θ, R_S is the thickness in Å, that constitutes a given spacing separating the two unit cell types (called here h, and k because either may be I or S). σ_S is the probability of occurrence of the spacing R_S separating h and k, and δ is the mean defect-free distance in Å (Ergun, 1970). As a practical matter, the summation can be terminated at approximately 7δ because the exponential weighting term is so small at that point that further terms of the sum are insignificant.

The formulation of Eq. 1 applies to a two-component system, in this case, illite and smectite layers. The total number of terms in the summation is equal to 2^N. The frequency term, σ_S, is calculated according to the principles of Markovian statistics. For example, if $P_I > 0.5$, and R = 1, then nearest neighbor ordering requires that $P_{S/I} = 1$, that is, given a smectite, the next layer must be an illite. The conservative relation here requires that

$$P_{S/I} + P_{S/S} = 1, \qquad (2)$$

because something must follow a smectite. This means that $P_{S/S} = 0$, that is, the layer pair smectite-smectite is forbidden. In a similar fashion, R = 4 statistics is exemplified by the relation

$$P_{SII/I} + P_{SII/S} = 1. \qquad (3)$$

If $P_I > 0.75$ and R = 4, then $P_{SII/I} = 1$ because the sequence $P_{SII/S}$ depicts the R = 3 condition and is not allowed. Following this logic, any spacing R_S that

contains the sequence SIIS has a σ value of zero. All non-zero values of σ occur for sequences like SIIISIIIISIIIIISIII. That is, all smectite layers must be separated by three or more illite layers. The abundances of sequences with more than three illite layers depends on P_I, and as P_I approaches unity, the illite sequences between smectite layers become very large. Only four transition probabilities have been discussed here, and there are many more. A complete treatment of these is beyond the scope of this report, and the interested reader should see Reynolds (1980). Figure 1 shows the definition of the illite and smectite layers and one possible stacking sequence. In this sequence, one of the spacings, R_S, is indicated.

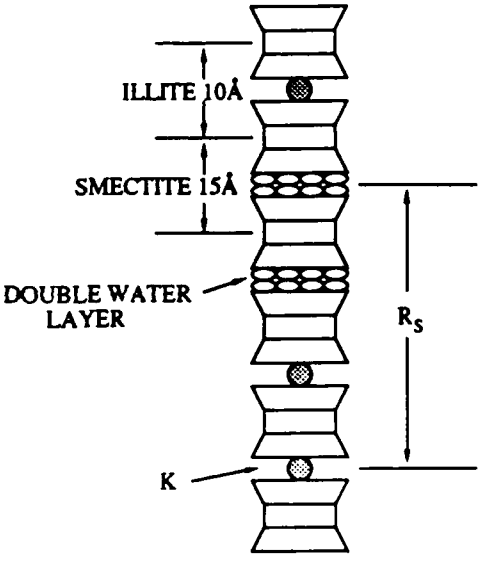

Figure 1. Assignment of illite and hydrated smectite layers and an example of a spacing, R_S.

Figure 2 shows the fundamental particles postulated by Nadeau *et al.* (1984). The three-layer shapes are the 2:1 silicate skeletons, and potassium (K) coordinates them. The surfaces of the particles are shown with a single layer of water or ethylene glycol, for the laboratory preparation. These particles, when stacked into aggregates, are separated by hydrated layers which are the smectite components. It is easy to see how ordering is accomplished with such a scheme. Consider a random stacking sequence of all of these layers. Then the presence of 10-Å particles will produce sequential pairs of hydrated interlayers. This condition is the random one because the sequence smectite-smectite is

present. For R = 3, only the 40-Å illite and thicker particles are allowed because this guarantees that all smectite (hydrated) interlayers are separated from each other by at least three K (illite) interlayer spaces. The crystallite is visualized as a random interstratification of these (and thicker) particles, the proportions of which determine the effective proportions of illite and smectite.

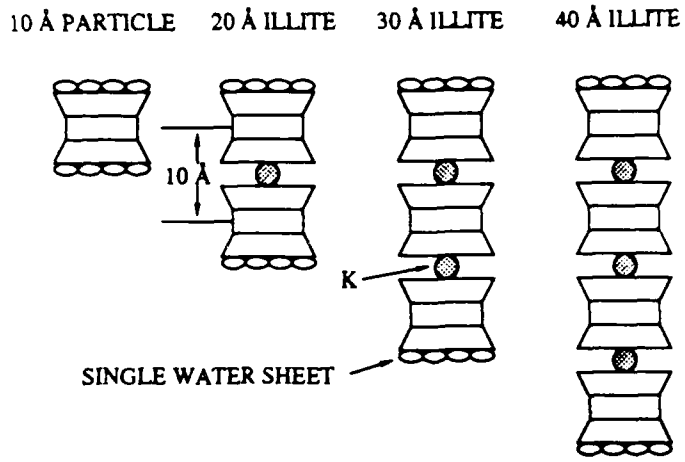

Figure 2. Examples of fundamental particles that stack to form mixed-layered illite/smectite crystallites, after Nadeau *et al.* (1984).

Calculation of the basal X-ray diffraction pattern is accomplished using Eq. 1, except that we now have a polycomponent, instead of a binary system. The number of components is equal to the number of different kinds of fundamental particles, and the σ terms are expressions for the proportions of the different kinds of fundamental particles, and the number of ways that they can be stacked to produce a given value for each of the spacings R_S. The scattering amplitudes, G, now refer to the amplitude of scattering, in the direction θ, for each of these fundamental particles. The problem is greatly simplified by the fact that the stacking sequences of the particles are random, but the difficulties of calculation are greatly increased by the very large number of terms that must be treated by Eq. 1. For, say, 5 components stacked in aggregates of 10, the number of different spacings that are generated is equal to 5^{10}, or about ten million. Because of the random stacking pattern, however, these can be grouped into sets, within which all members have equal probabilities of occurrence and the same value of R_S. Nevertheless, the calculations require many hours on a mainframe computer or several minutes on a Cray II. Calculations for mixed-

layered illite/smectite require that the fundamental particle frequency distribution be known, and this must be measured by means of transmission electron microscopy. Paul Nadeau has collaborated with us on this matter and has provided us with such distributions for a number of illite/smectite samples which have been and are in the process of being modeled.

The critical question arises: how do the distribution of spacings R_S differ between the Markov statistical model and the fundamental particle approach? We are in the process of studying this question now, but in general terms, we can state that they can be different. The Markov model is completely specified by three parameters--P_1, the Reichweite and δ. The fundamental particle model requires δ also, but in addition, it needs an estimation of the proportions of all of the different kinds of fundamental particles that make up the structure. For the most general case, any proportions seem possible, and then there will be marked differences between the distributions of spacings in the two models. However, the fact that the Markov model works so well suggests that there are important natural constraints on the proportions of fundamental particles in different illite/smectites, each of which represent different points on the continuum of the smectite--illite reaction progress.

RESULTS

Results described here are summarized from Tellier and Reynolds (1987). Figure 3 shows a comparison between experimental and calculated diffraction patterns for the ethylene glycol-solvated Zempleni hydrothermal illite/smectite. CuKα radiation is assumed for this and the other diffraction patterns shown here. The calculated pattern was prepared by means of the computer program NEWMOD (Reynolds, 1985) for the case 87% illite, R = 3. NEWMOD is based on the Markovian model (Eq. 1 and Fig. 1). The largest discrepancies between the two occur at low diffraction angles. The low-angle "background" is too intense on the calculated case, and this condition is invariably present for minerals with this composition and ordering type. In addition, the strong reflection near 10 °2θ is unacceptably displaced. Figure 4 reiterates the experimental pattern and shows the pattern calculated by FPMOD which performs the calculations on the basis of the fundamental particle concept of Nadeau *et al.* (1984). FPMOD produces a marked improvement in the agreement between calculated and experimental results.

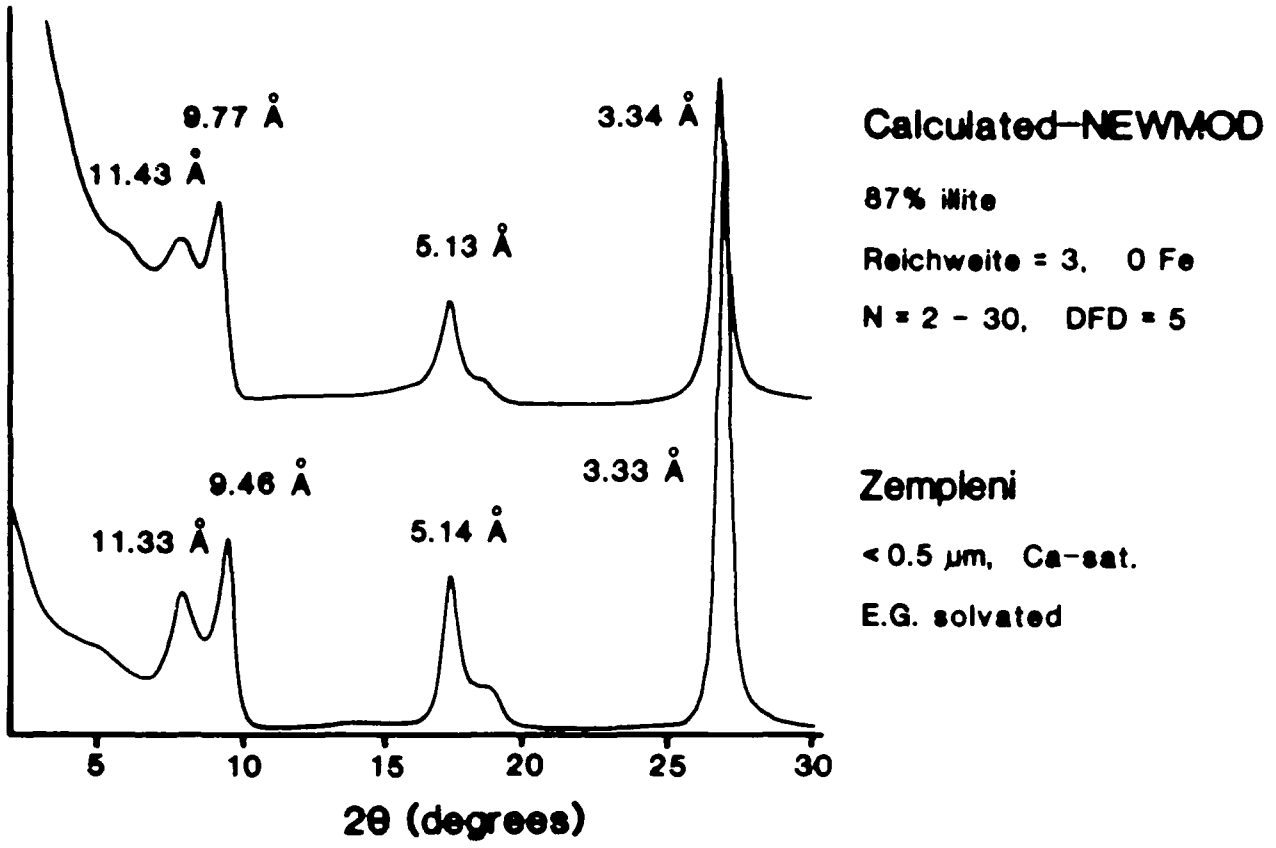

Figure 3. Basal X-ray diffraction patterns for the ethylene glycol-solvated Zempleni illite/smectite (CuKα radiation). The calculated pattern is based on Markovian statistics (NEWMOD, Reynolds, 1985). The defect-free distance (DFD) = 5 unit cells.

Figures 5 and 6 show comparisons for a more expandable illite/smectite which is an Ordovician potash bentonite. Again, the agreement between experimental and calculated results is improved by the calculations according to the fundamental particle theory. These results, and others not shown here, lead us to conclude that the approach of Nadeau and co-workers produces more realistic calculated X-ray diffraction patterns for mixed layered illite/smectite. This finding implies the essential correctness of their model, consideration of which suggests that the transformation of smectite to illite takes place by the dissolution of smectite layers, and the growth of illite fundamental particles of increasing thickness.

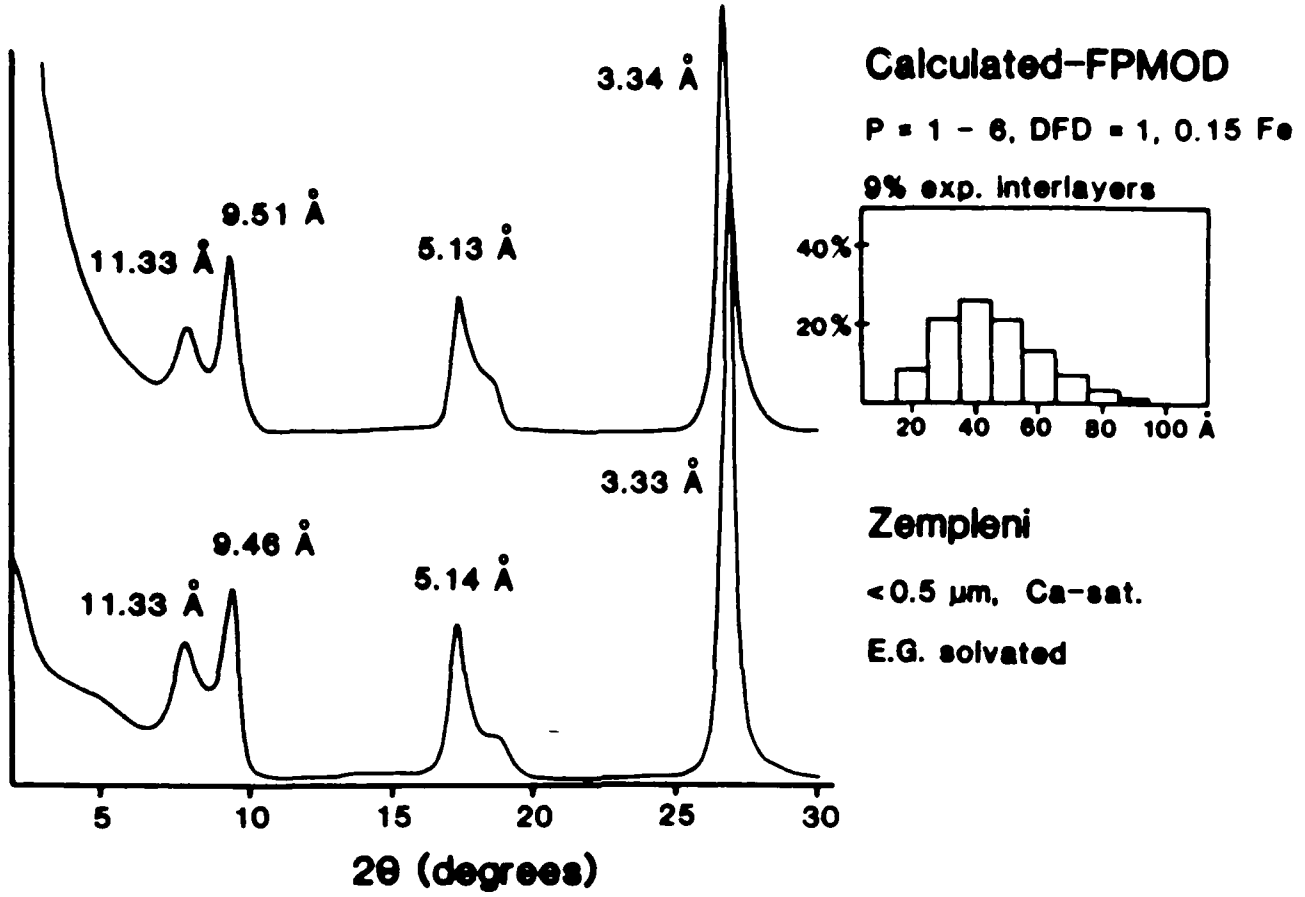

Figure 4. Basal X-ray diffraction patterns for the ethylene glycol-solvated Zempleni illite/smectite (CuKα radiation). The calculated pattern is based on a distribution of fundamental particles shown by the inset. The mean defect-free distance is one particle.

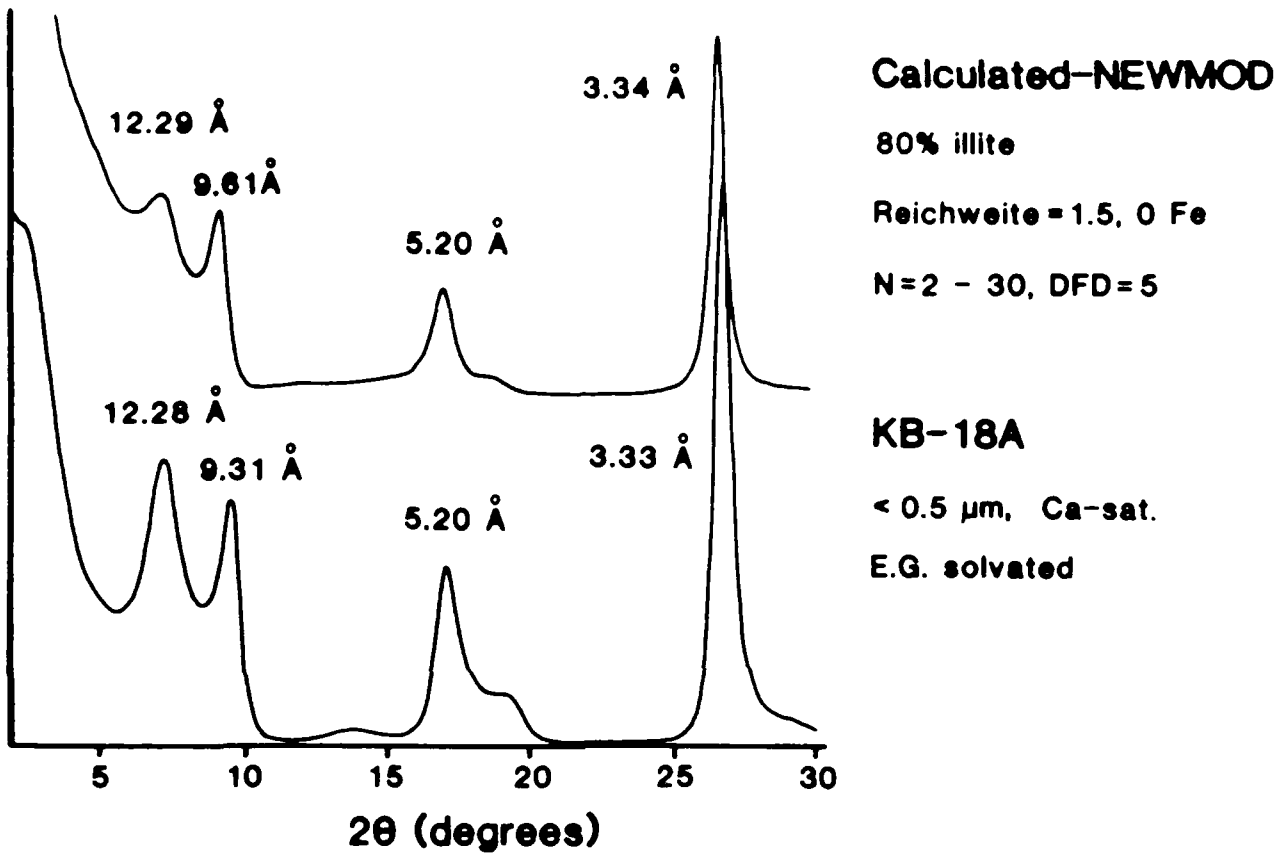

Figure 5. Basal X-ray diffraction patterns for the ethylene glycol-solvated potash bentonite (CuKα radiation). The calculated pattern is based on Markovian statistics (NEWMOD, Reynolds, 1985). The defect-free distance (DFD) - 5 unit cells.

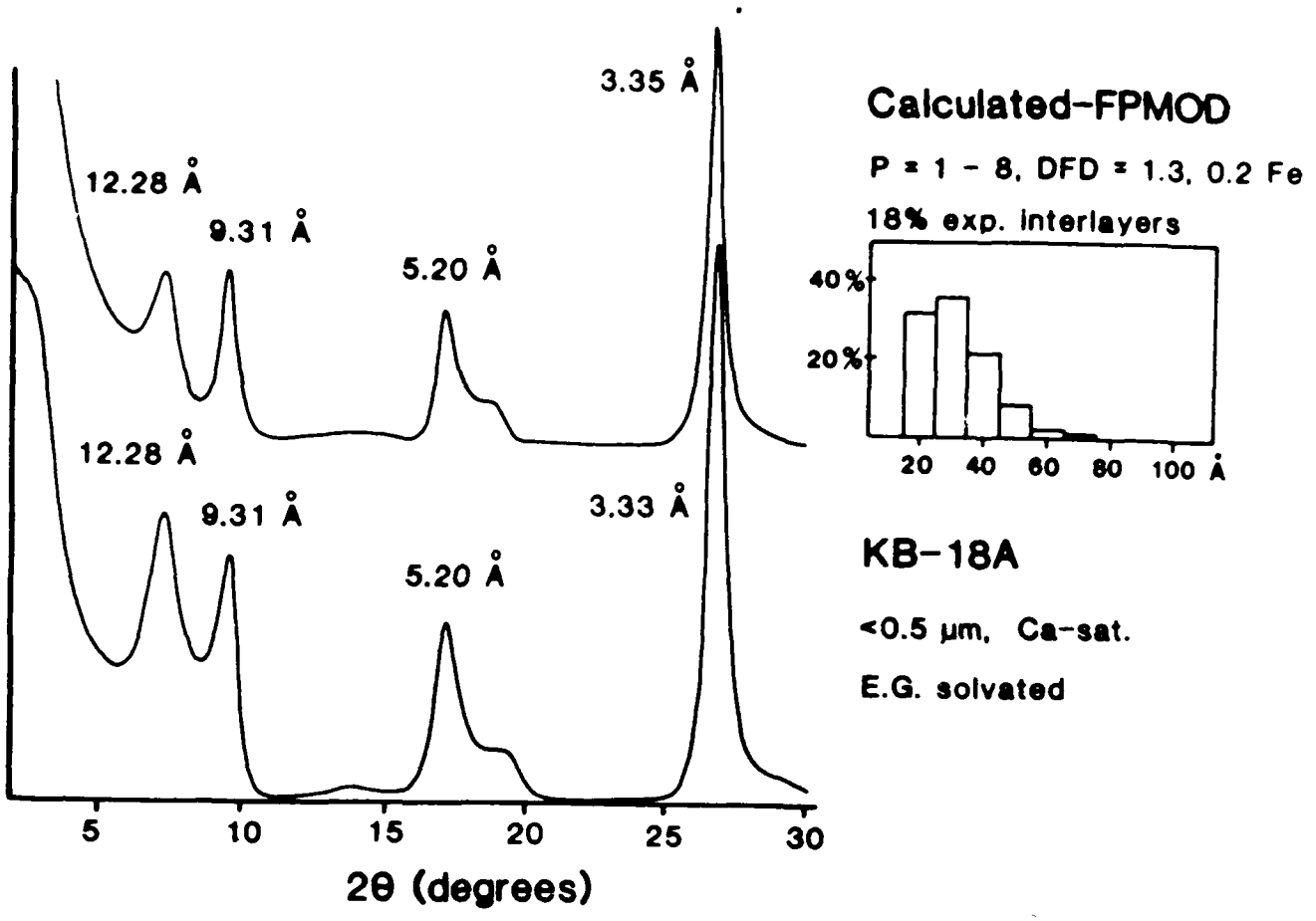

Figure 6. Basal X-ray diffraction patterns for the ethylene glycol-solvated potash bentonite (CuKα radiation). The calculated pattern is based on a distribution of fundamental particles shown by the inset. The mean defect-free distance is 1.3 particles.

MOST IMPORTANT FINDINGS

1. Calculated X-ray diffraction patterns for illite-rich, long-range ordered illite/smectite are more realistic if the calculations are based on the random interstratification of different thicknesses of fundamental illite particles that adsorb water or ethylene glycol at their interfaces.

2. The fundamental particle model tested was suggested and described by Nadeau *et al.* (1984). Our work provides some confirmation of their hypothesis.

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